



Materials

Wholly Aromatic Ether-Imides as n-Type Semiconductors

Some of the compounds exhibit promising electron-transport properties.

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Some wholly aromatic ether-imides consisting of rod-shaped, relatively-low-mass molecules that can form liquid crystals have been investigated for potential utility as electron-donor-type (n-type) organic semiconductors. It is envisioned that after further research to improve understanding of their physical and chemical properties, compounds of this type would be used to make thin-film semiconductor devices (e.g., photovoltaic cells and field-effect transistors) on flexible electronic-circuit substrates.

This investigation was inspired by several prior developments:

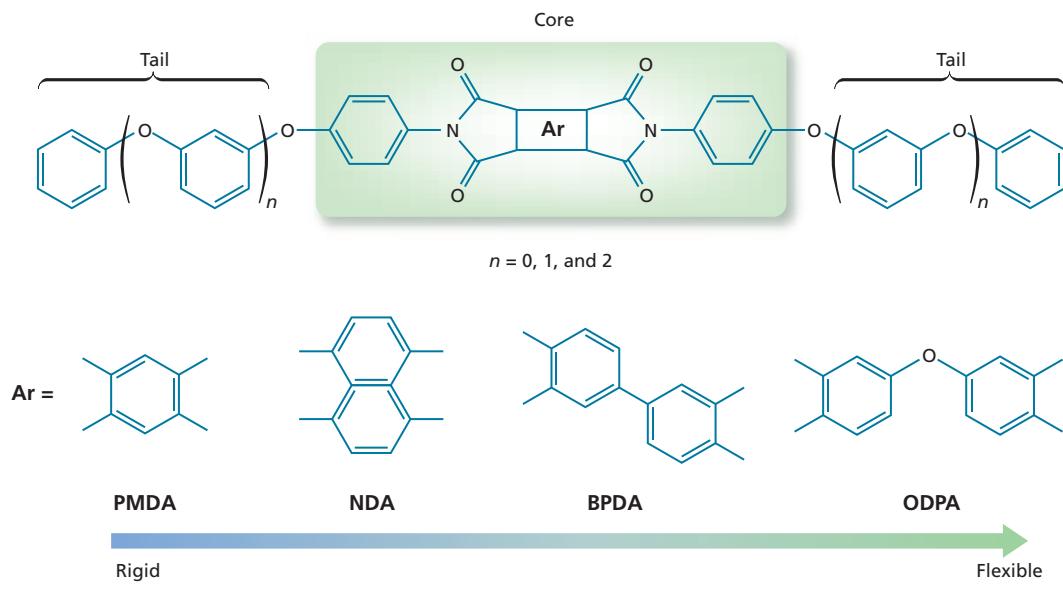
- Poly(ether-imides) [PEIs] are a class of engineering plastics that have been used extensively in the form of films in a variety of electronic applications, including insulating layers, circuit boards, and low-permittivity coatings.
- Wholly aromatic PEIs containing naphthalene and perylene moieties have been shown to be useful as electrochromic polymers.
- More recently, low-molecular-weight imides comprising naphthalene-based molecules with terminal fluorinated tails were shown to be useful as n-type

organic semiconductors in such devices as field-effect transistors and Schottky diodes.

Poly(etherimide)s as structural resins have been extensively investigated at NASA Langley Research Center for over 30 years. More recently, the need for multi-functional materials has become increasingly important. This n-type semiconductor illustrates the scope of current work towards new families of PEIs that not only can be used as structural resins for carbon-fiber reinforced composites, but also can function as sensors. Such a multi-functional material would permit so-called *in-situ* health monitoring of composite structures during service. The work presented here demonstrates that parts of the PEI backbone can be used as an n-type semiconductor with such materials being sensitive to damage, temperature, stress, and pressure. In the near future, multi-functional or “smart” composite structures are envisioned to be able to communicate such important parameters to the flight crew and provide vital information with respect to the operational status of their aircraft.

Prior attempts to make electronic devices based on n-type organic semiconductors had failed because permeation by oxygen from air limited the lifetimes of the devices. In this development, the close molecular packing in the fluorinated imides is believed to have extended the lifetimes and improved the performances of the devices by preventing permeation by oxygen and moisture.

On the basis of promising results in the aforementioned prior developments and of other considerations, it was conjectured that for the purpose of developing n-type organic semiconductors, wholly aromatic imide-based mesogenic (liquid-crystal-forming) compounds would offer several advantages over non-mesogenic compounds. Liquid crystals are well known for their outstanding barrier properties, and when designed properly, their unique packing motifs could result in increased charge-carrier mobilities. Conceivably, rigid aromatic dianhydrides terminated with appropriate aryl-ether amines could have the requisite liquid crystalline properties. Prior to this investigation, some research groups had reported on



Ether-Imide Compounds investigated for utility as n-type semiconductors have this generic molecular structure.

low-molecular-weight imide-based liquid crystals, but these compounds contain aliphatic units, which lack the oxidative stability necessary for semiconductor applications.

The generic molecular structure of the wholly aromatic ether-imide compounds of this investigation is a classic "tail-core-tail" structure, which is denoted by the term "calamitic" in the liquid-crystal art. In the generic molecule, the core contains one of four dianhydrides with a *p*-phenylamine at each end. The dianhydrides are pyromellitic dianhydride (PMDA); 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA); 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), and 3,3',4,4'-oxydipthalic dianhydride (ODPA). The tails are members of a homologous series of meta-substituted aryl-ethers. Each tail is the para substituent on the *p*-phenylamine (see figure).

This generic molecular structure was chosen for the following reasons: The *p*-

phenylamine functionality increases the length of the core beyond that of the rigid di-imide portion, while the bulky meta-substituted aryl-ether tails have some flexibility. Increasing the numbers of meta-substituted aryl units in the tails reduces melt transition temperatures and increases solubilities. Also, the tails stabilize the molecular orientations necessary for mesophase formation. Aryl-ether flexible tails had not been used previously as flexible tail segments in liquid crystals, and in comparison with alkyl or alkoxy flexible tails, aryl-ether tails have more breath, which keeps the overall diameters of mesogens more nearly uniform.

In the investigation, monofunctional amines (destined to become tails) were synthesized by various techniques, then combined with the dianhydrides (destined to become the cores) in one-step solution imidization procedures to obtain the desired ether imides. These compounds were examined for tempera-

ture-dependent phase behavior by means of optical microscopy and x-ray diffraction, and cyclic voltammetry was used to characterize redox behavior. Absorption spectroscopic measurements were also performed on dilute solutions of the compounds. Of these compounds, those containing NDA and BPDA in the cores were found to have electron-transport properties suitable for n-type semiconductors. Of all the compounds tested, only one containing NDA in the core clearly exhibited a tendency toward formation of liquid crystals. This is the first example, known at the time of the tests, in which a mesophase was detected in a wholly aromatic ether-imide compound.

This work was done by Erik Weiser and Terry L. St. Clair of Langley Research Center; Theo J. Dingemans (ICASE); Edward T. Samulski and Gene Irene of the University of North Carolina at Chapel Hill. Further information is contained in a TSP (see page 1).

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Carbon-Nanotube-Carpet Heat-Transfer Pads

The compliance and high longitudinal thermal conductivity of carbon nanotubes are exploited.

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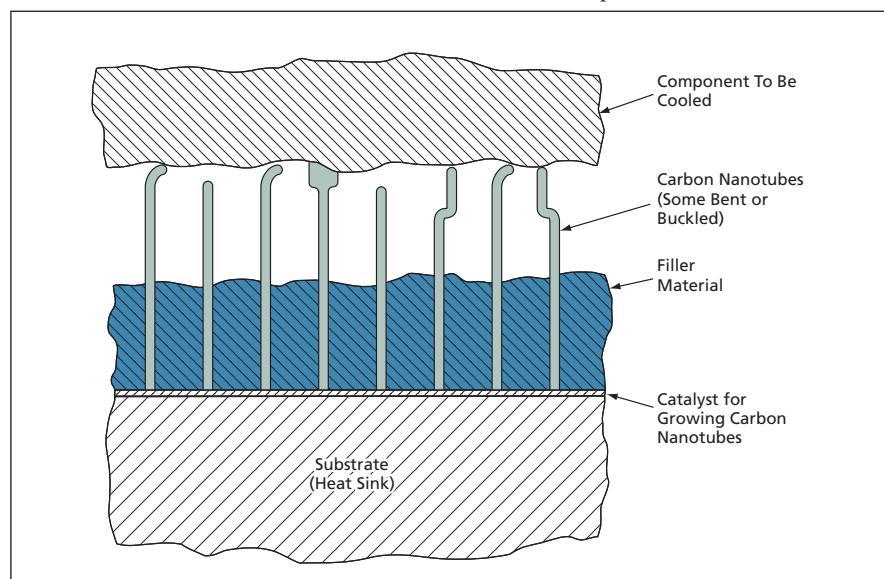
Microscopic thermal-contact pads that include carpetlike arrays of carbon nanotubes have been invented for dissipating heat generated in integrated circuits and similarly sized single electronic components. The need for these or other innovative thermal-contact pads arises because the requisite high thermal conductances cannot be realized by scaling conventional macroscopic thermal-contact pads down to microscopic sizes. Overcoming limitations of conventional thermal-contact materials and components, the carbon-nanotube thermal-contact pads offer the high thermal conductivities needed to accommodate the high local thermal power densities of modern electronic circuits, without need for large clamping pressures, extreme smoothness of surfaces in contact, or gap-filling materials (e.g., thermally conductive greases) to ensure adequate thermal contact. Moreover, unlike some conventional thermal-contact components, these pads are reusable.

The figure depicts a typical pad according to the invention, in contact with a rough surface on an electronic component that is to be cooled. Through reversible bending and buckling of carbon nanotubes at asperities on the rough sur-

face, the pad yields sufficiently, under relatively low contact pressure, that thermal contact is distributed to many locations on the surface to be cooled, including valleys where contact would not ordinarily occur in conventional clamping of rigid surfaces. Hence, the effective thermal-contact

area is greater than that achievable through scaling down of a macroscopic thermal-contact pad.

The extremely high longitudinal thermal conductivities of the carbon nanotubes are utilized to conduct heat away from potential hot spots on the surface to be



Carbon Nanotubes Bend and Buckle to accommodate roughness of the surface of the component to be cooled. The high longitudinal thermal conductivity of carbon nanotubes is exploited to conduct heat into the heat sink.